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(Article begins on next page)

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Conventional and microwave assisted hydrolysis of urban biowastes to added value lignin-like products

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Abstract

The hydrolysis of five fermented water insoluble urban wastes is shown to convert the insoluble recalcitrant organic lignin-like fraction to added value soluble lignin-like products in high yields. The hydrolysate products are mixture of complex polymeric molecules which maintain the memory of the proximates of the pristine materials..For a composted biowaste, taken as case study, a process feasibility study comparing the microwave (MW) assisted versus the conventional (CON) reaction is reported. Product yields and quality are investigated as a function of four process parameters: i.e. pH (8-13), temperature (60-200 °C), and liquid-solid w/w ratio (4 and 10) and contact time (1 min-4 h). Microwave heating allows obtaining the same products, and in the same yields, as conventional heating in 1-2 order magnitude lower time. It is possible to achieve 50-60 % yields of soluble lignin-like products at relatively low temperature ≤ 100 °C. The obtained yield vs. temperature trend indicates that even higher yields may be obtained at higher temperature. The potential scalability of MW assisted versus CON hydrolysis to industrial level is discussed in relation to the reaction rate and reactor cost. The results offer worthwhile research scope to compare MW and CON heating for the hydrolysis of other fermented and non fermented as collected biowastes. .

Keywords: microwave, conventional heating, hydrolysis, urban biowastes, lignin, hydrolysates

Abbreviations: a (intercept), b (slope), Cal (aliphatic carbon), CON (conventional), COW (carboxyl carbon), CV (compost of home gardening and park trimmings residues), F (urban sewage sludge), CVD (compost of 33/67 w/w FORSUD/V mix), CVDF (compost of 35/55/10 w/w/w FORSUD/V/F mix), CVF (compost of 35/10 w/w V/F mix), FORSUD (digestate from food wastes anaerobic fermentation), FW (food wastes), l/s (liquid-solid ratio), IOR (insoluble hydrolysate), MW (microwave), NMR (nuclear magnetic resonance), NR (ammine carbon), OCO (anomeric carbon), OMe (methoxy carbon), Ph (aromatic C), PhOY (phenol and/or phenoxy carbon), RO (alkoxy carbon), SBO (soluble bio-organic substances), r (regression coefficient), SEC-MALS (size exclusion chromatography- multiangle laser light scattering), t (contact time), T (temperature), V (home gardening and park trimmings residues), VS (volatile solids), X (ratio of total carbon to sum of methoxy, ammine and carboxyl carbon), Y (C or N % yield)

Introduction

The removal¹⁻⁴ and conversion of natural lignin, or lignin-like matter, to added value products⁵ is a critical point and a major issue for the valorization of dedicated non-food energy crops or residual biomass as source of renewable fuels and chemicals. This is due to the fact that lignin inhibits fermentation microorganisms and is an insoluble recalcitrant material withstanding biochemical and chemical treatment. Current biomass treatment technology,^{1, 6} mainly focused to the production of biofuel by fermentation, such as biogas and bioethanol, adopts a variety of biomass pretreatment methods to remove lignin from the fermentable fraction and/or processes the residual lignin fraction by combustion, pyrolysis, hydro cracking, or aerobic fermentation. Respectively, these processes convert the chemical energy to thermal and electric energy, produce hydrocarbons and other platform chemicals, and compost which is use for landscaping and/or soil fertilization.⁷ Yet, the biowaste lignin fraction has further potential⁸ which can be exploited by low energy consumption chemical technology. Lignin is the second most abundant organic component next to cellulose in the vegetable world. The emerging biomass refinery industry will inevitably generate an enormous amount of lignin. Development of selective biorefinery lignin-to-bioproducts conversion processes will play a pivotal role in significantly improving the economic feasibility and sustainability of biofuel production from renewable biomass.

Recently, several papers have reported that the recalcitrant lignin-like fraction of fermented municipal biowaste is a cost effective source of soluble bio-organic substances (SBO) that can find application in diversified fields; e.g. in the formulation of detergents textile dyeing baths, flocculants, dispersants and binding agents for ceramics manufacture,⁹ emulsifiers,¹⁰ auxiliaries for soil/water remediation¹¹⁻¹³ and enhanced oil recovery,¹⁴ nanostructured materials for chemical^{15, 16} and biochemical catalysis,¹⁷ plastic materials,¹⁸ soil fertilizers and plant biostimulants for agriculture,¹⁹ and animal feed supplements.^{20, 21} Two patent applications for production processes and products have been recently filed.^{22, 23} These results, mainly focused on products' performance, offered worthwhile scope for process development.

The present work reports the results of a process feasibility study aiming to collect data for upgrading and validating at EU TRL6-7 the hydrolysis of fermented biowastes for the production of the above SBO. Five different samples were taken from the process streams of Acea Pinerolese Spa waste treatment plant located in Pinerolo (TO), Italy. The plant treats the bio-wastes collected from an area of 2,200 km² populated by 800,000 inhabitants distributed over 100 municipalities. The processed biowaste amounts to about 50,000 ton year⁻¹. They comprise the organic humid fraction from separate source collection containing animal and vegetable food wastes (FW) from urban consumption, home gardening and park trimmings residues (V) and urban sewage sludge (F). The bio-wastes are processed through two integrated steps comprising anaerobic and aerobic digestion. The anaerobic digestion yields biogas and a solid digestate (FORSUD) containing residual organic matter not converted to biogas. The biogas is the most valuable product.⁹ Indeed the plant represents a typical example of the most advanced municipal biowaste treatment technology developed based mainly on the fuel value of bio-wastes. The total amount of the plant biogas is more than enough for cover the plant energy consumption. Electrical power for three total MWe is obtained through three heat engines fed with the biogas. The heat engines exhaust gas is used to produce both hot water and diathermal oil for use in the plant steam generator. The produced electrical power supplies the plants needs and exceeding energy sold to electrical network. The plant guarantees also 6 MW thermal power enough for internal use and, since 2008, for part of the heating requirements of the nearby Pinerolo town residential and commercial districts.

For the Acea plant, the FORSUD material recovered from the biogas production has little value and requires disposal. This is accomplished by aerobic fermentation. To this scope, FORSUD is mixed the V and/or F biowastes, and then composted to yield the following materials: CV being V composted for 365 days respectively; CVDF being a 35/55/10 w/w/w FORSUD/V/F mix composted for 110 days; CVD being a 33/67 w/w FORSUD/V mix composted for 110 days; CVF being a 35/10 w/w V/F mix composted for 110 days. Unfortunately, the composted materials have low market value. Indeed, the plant revenue has been reported⁹ to be generated 57 % from tipping fees and energy recovery incentives, 42 % from the biogas sale, and less than 1 % from the compost sale. Based on the above published work,⁹⁻²¹ the hydrolysis of the plant digestate and/or compost offered the opportunity to valorize these materials as source of added value SBO. Processing the fermented materials prospected the possibility to convert a waste treatment plant producing mainly biogas into a biorefinery producing fuel and marketable chemical products. Under this perspective, the hydrolysis of non fermented as collected urban biowastes was not considered in the present work.

As reported hereinafter, for the hydrolysis of the above fermented biowastes product yields and quality were investigated as a function of four process parameters. These were varied in the following ranges: i.e. pH from 9 to 13, temperature (T) from 60 to 200 °C, and liquid-solid w/w ratio (l/s) from 4 to 10 and contact time (t) from 1 min to 4 h. The objective of the experimental plan was twofold: (i) to obtain products which maintained as much as possible the structural memory of the natural organic matter present in the pristine biomass, but were soluble in water; (ii) to investigate products' yield as a function of the required process energy and reactor cost. For this reason, the study has included the comparison of conventional (CON) and microwave (MW) heating.

Use of microwaves for chemical reactions began on a commercial scale 50 years ago. However, the interest on MW for biomass process intensification dates back to the first decade of the 21st century.²⁴ Compared to CON heating, non-conventional energy sources such as MW can dramatically enhance reaction rates in organic synthesis²⁵ and thus allow reducing reagents contact time²⁶ and reactor volume. This, in principle, is an important step toward the construction of plants that are more compact, cost-effective and safer.²⁴ Several case studies have already been published on the application of MW for biomass processing. As an example of disrupting recalcitrant lignocellulosic structures, Hu and Wen²⁶ have reported that the MW-assisted alkali treatment of switch grass is more efficient than CON heating.

The combined use of alkali and MW, compared to CON heating, has been reported for the pretreatment of several vegetable biomasses^{4b, 26} Higher reaction rate and/or yield are reported by MW compared to conventional heating. To the knowledge of the present work authors, no study comparing MW and conventional heating for the alkaline hydrolysis of fermented municipal biowaste has been published. For the type of biowaste and the applied treatment technology, the present work addresses directly important green chemistry issues. Indeed, for their world wide ready and easy availability, municipal biowastes are a negative cost²⁷ source of renewable exploitable organic C to recycle to the chemical industry and agriculture. Also, environmental and/or economic benefits may derive from the use of MW and the consequent potential reduction of plant size and land space occupation.

Results and discussion

The experimental work comprised two phases, which were respectively dedicated to the chemical characterization of the pristine biomass and its hydrolysis products obtained by conventional (CON) heating, and to the process feasibility study comparing MW and CON heating. Several products

were obtained in the first phase in a specifically designed and built pilot plant. The size of this plant could yield product quantities suitable for on field application studies in close to real operational conditions. Such preliminary experiments were essential to assess whether, depending on the products performance, a process development study was worthwhile to be carried out.

Pristine biomass and product characterization

The hydrolysis of the above digestate and composts was performed in the pilot plant described in the experimental part at pH 13, 60 °C and 4 l/s ratio. Under these conditions two products were obtained, hereinafter named the soluble (SBO) and insoluble (IOR) hydrolysates. The purpose of these runs was to have a range of different biowastes and products which allowed to achieve three objectives: (i) to set up an analytical protocol for the characterization of the chemical composition of products and sourcing materials, (ii) to investigate the relationship between the product and sourcing material chemical nature, (iii) to identify a simple analytical index which could be meaningfully used in process feasibility studies requiring many runs in order to assess the product quality without excessive analytical effort.

The achievement of the above three objectives, prior to carrying on the process feasibility study, was necessary because of the complexity of the chemical nature of the products and sourcing biowastes. Indeed, the organic matter of these materials of biological origin is a mixture of molecules, differing for molecular weight and chemical composition. In addition to this, the pristine sourcing materials and the SBO and IOR products differ for water solubility; i.e. the sourcing material and the IOR are insoluble, the SBO is soluble. The above municipal bio-wastes are constituted by the main proximates of vegetable and animal food species, i.e. cellulose, hemicelluloses, lignin, proteins, fats. As a consequence of biochemical and chemical treatment, these proximates undergo significant structural changes. Thus, the digestate, the composts, and their hydrolysates contain organic moieties which keep the memory of the pristine proximates' chemical nature, but are different than those in the native materials. Established methods for the analytical determination are not specific. They allow to obtain estimates of proximates' content, but do not provide any information on their organic moieties. As an example, the SBO were characterized according to the methods²⁰ established for feed analyses by A.O.A.C. to yield the proximate compounds' concentration values reported in Table 1. However, more meaningful chemical information (Table 2-5) was obtained by analyzing the mineral content and characterizing further the organic fraction by its type and content of C types and functional groups. According to Table 1 the investigated SBO appear composed mostly by protein, lignin, cellulose and silicates, whereas fats are at rather low concentration. The C types and functional groups concentration values (Table 4), calculated from ¹³C NMR spectroscopy, potentiometric titration and C and N micro analytical experimental data, show that in reality the cellulose material is quite low. This is demonstrated by the rather low fraction (3-5 %) of the anomeric (OCO) C. This result is consistent with the product source having undergone anaerobic and/or aerobic fermentation. Due to this treatment and the subsequent hydrolytic reaction of the recovered material, the SBO products cannot be classified simply as mixture of the proximate compounds listed in Table 1. They should rather be viewed as biodegraded lignocellulose matter containing Table 4 C types and functional groups, which represent the memory of the parent proximate compounds present in the sourcing vegetable or food waste material. Under these circumstances, all investigated materials were characterized by the content of volatile solids (VS) and elemental C and N (Table 2), and by ¹³C NMR solid state spectroscopy to obtain the C types and functional group content reported in Table 4. For the SBO hydrolysates, it was possible to obtain also molecular weight data by SEC-MALS analysis and the further breakdown of the functional groups shown in Table 5. These same measurements could not be performed for the pristine digestate and composts, and for IOR, due to their insolubility.

The collected data confirm the polymeric nature of all materials. Table 5 shows that the soluble hydrolysates (SBO) have weight average molecular weight of 74-164 kDa and dispersivity index of 1.9-3.4. Hydrolysis is expected to break chemical bonds in the pristine digestate and compost materials. Thus, these materials are expected to have even higher molecular weights than SBO. For their insolubility, the IOR products are also likely to have higher molecular weight than SBO. The VS data in Table 2 show that both the pristine biomass samples and their hydrolysates are not entirely constituted by organic matter. They contain also a mineral fraction, ranging from 15 to 70 %. Table 3 reports the analytical for the main and trace mineral elements. It may be observed that, consistently with the VS data in Table 2, each element is present in SBO at lower concentration than in the sourcing digestate or compost, and in the IOR hydrolysate. The only exception is K. All mineral elements, except K, are contributed by the pristine digestate and compost. Potassium is added with the alkali to perform the hydrolysis of these materials. The data show that while all pristine elements are retained mainly by the insoluble IOR products, K is preferentially bonded to the soluble reaction product. Table 4 shows that the organic fraction of all materials contains aliphatic and aromatic C moieties substituted by a variety of functional groups. These C moieties represent the chemical memory of the native proximates constituting the pristine as collected vegetable and animal biowastes. Specifically, the anomeric (OCO) and alkoxy (OR) functional groups indicate the presence of polysaccharide matter, the aromatic (Ph) and phenol/phenoxy (PhOY) groups indicate the presence of lignin-like matter, and the carboxyl (COX) and amino (NR) groups indicate the presence of proteinaceous moieties surviving the fermentation processes. It should however be considered that these moieties do not indicate separate proximate. They most likely arise from polysaccharide, proteins and lignin bonded to each other. Generally it may be observed that, compared to pristine FORSUD, the pristine compost samples contain more lignin-like and less protein C. This is also reflected in the higher C/N ratio (Table 2) of the compost samples. The difference between the digestate and the compost samples is likely to be contributed by the anaerobic versus aerobic fermentation conditions, the latter leading to further protein degradation and N loss.

Compared to the sourcing digestate and composts, the SBO and IOR hydrolysates exhibit different distributions of C, N, and organic moieties. Table 2 show that each SBO has higher VS, C and N content, and lower C/N ratio than its sourcing biomass. On the contrary, each IOR has lower, VS, C and N, and higher C/N ratio. The hydrolysis therefore seems to occur with significant selectivity. It converts to soluble matter more organics than minerals, and molecules containing a relatively lower C/N ratio. Table 4 shows that, compared to the pristine biomass, each SBO exhibits a marked decrease of OR and OCO C and a marked increase of aliphatic, aromatic and carboxyl C. The IOR shows roughly opposite changes. Thus it seems that hydrolysis occurs at O=C-OR functional groups^{4b, 28} present in the pristine biomass, with R being a polysaccharide residue. Under the assumption that no ester functional groups are present in SBO, the potentiometric titration of SBO, coupled to the data in Table 2 and 4, allows to obtain the breakdown of the OR+OMe and of the COY C and to calculate separate values for OR, OMe, COO⁻ and =O-C-N C. The results in Table 5 show indeed that most of carboxyl C in SBO is in free carboxylate form, which supports the hypothesis of hydrolysis of ester functional groups present in the pristine biomass. The data shows that SBO contains also amide functional groups, and that in all cases, except one, most of the total OMe and NR C in Table 4 is accounted by carbon bonded to amine groups. Amide and amine groups are expected to account for the lower C/N ratio of the SBO compared to the pristine biomass and IOR. Indeed, the ratio (X) of total C to the sum of NR and COY groups in Table 2 has been found to correlate nicely with the C/N values in Table 2 according to the equation

$$C/N = a + b X \quad (1)$$

for which $a = -1.81 \pm 1.95$, $b = 2.60 \pm 0.39$, and the regression coefficient (r) = 0.8773.

Process feasibility study: scope and investigated parameters

For the process feasibility study, the CVD biomass was chosen. At the time of this study, CVD was being produced by the Acea Pinerolese plant supplier. From the runs performed in 500 L pilot plant aiming to the SBO chemical nature characterization and performance assessment in the published⁹⁻²¹ diversified applications (see Introduction), it soon became evident that the most critical process step was the hydrolysis reaction. This was due to the recalcitrant nature of the lignin-like organic matter. The aim of the process study was to find out the reaction experimental conditions which allowed obtaining the highest SBO yield, while maintaining the organic moieties responsible of the product performance, as assessed in the product characterization study. To this purpose, the investigated reaction parameters were pH, *l/s*, *t*, and *T*. Laboratory CON and MW heated reaction flasks were used. Process material balance was based on VS, C and N % recoveries with the SBO and IOR products, relatively to the pristine CVD. The C/N parameter was used as index of the effect of the reaction parameters on the product chemical nature.

Preliminary hydrolysis runs, performed by either MW or CON heating, showed a strong effect of pH on the chemical nature and yield of SBO. The product yield was 2-5 % for the reaction performed at pH in the 9-12 range. At pH 13, the SBO C yield increased abruptly sevenfolds. Also, the products obtained at pH 9-12 were characterized by low 3.2-4.2 C/N values, whereas those obtained at pH 13 had 7.89 C/N. By comparison, the pristine CVD sample had 10.8 C/N. The 7.89 C/N value of the SBO obtained from the hydrolysis of CVD at pH 13 is consistent with the average 8.29 ± 0.86 C/N value of the SBO isolated from the compost materials in Table 2. The 3.2-4.2 C/N values of the SBO obtained from the hydrolysis of CVD at pH 9-12 indicate that the chemical nature of the products obtained at pH 9-12 is very different from that of the SBO products in Table 2. It appears that at pH 9-12 the SBO product contains more proteinaceous matter than at pH 13. Similar pH effect on products chemical nature and yields have been reported in the MW assisted alkaline hydrolysis of recalcitrant soil organic matter.²⁸ In the case of the digestate and compost materials hydrolyzed in the present work, the results obtained for hydrolysis carried out at different pH values propose new research scope for investigating the chemical nature and properties of the products obtained at pH 9-12. However, since all previously published work has been carried out on the performance⁹⁻²³ of the products obtained at pH 13, all other runs in the present work were performed at pH 13. Figures 1-3 and Table 6 and 7 report the results for the reaction performed at pH 13 by CON and MW heating.

The CON heating runs

Based on literature,²⁵ the major difference between reactions performed by CON and MW heating was expected the slower reaction rate of the one performed by CON. Thus, the effect of *t* on the SBO yield was first investigated in the CON runs at variable *T* in the 22-100 °C range and *l/s* 4. The results are reported in Fig.1 and 2. Fig.1 shows that, at each temperature, upon increasing *t*, the SBO VS% yield tends to an asymptotic value. This is reached at about 240 minutes. Also, the SBO VS yield clearly increases upon increasing *T*. Fig.2 shows the tridimensional plot of VS versus *t* and *T* and the data surface fitting according to the following Eq. 2

$$VS \% = c + a t + b T \quad (2)$$

Table 6 reports the results of the regression analysis performed according to this equation. It may be observed that the effect of temperature is six fold higher than that of the contact time.

Table 7 reports the maximum C and N % yields, calculated based on the recovered weights and C and N microanalyses for both the SBO and IOR products. For the SBO data obtained at 240 min *t*, 4 *l/s*, and *T* varying from 22 to 100 °C (runs 1 through 4), the linear regression yields the following equation:

$$Y = a + b T \text{ (3).}$$

The constants and regression coefficient values for $Y = C$ or $N \%$ are reported in Table 6. The high correlation coefficients of Eq 2 and 3 demonstrate that the observed yields vs. t and T trends are highly significant.

The effect of the l/s ratio can be evaluated upon comparing the SBO C and N yields (Table 7) in runs 4, 5 and 6.6. At 100°C , the $C \%$ yield is 38.1 at l/s 4 (run 4) and 42.3-48.8 % at l/s 10 (runs 5 and 6.6). At the same T , the N yield is 47.1 % at l/s 4 (run 4) and 52.55-60.95 % at l/s 10 (runs 5 and 6.6). The yield values in run 4 are apparently lower than those in runs 5 and 6.6. However, based on Eq 3 and on the coefficients' standard error (Table 6), it can be estimated at 95 % confidence level that the SBO C and N yields at l/s 4, 100°C and 240 min t may run from 27.0 to 46.8 %, and from 37.1 to 56.2 %, respectively. Thus, no definite effect on SBO yield can be assessed upon increasing the l/s ratio from 4 to 10.

The data for the CON runs 1 through 6.6 (Table 7) also shows no effect of the t , T and l/s upon the products C/N values. The average values are 8.69 ± 0.20 for SBO C/N and 14.4 ± 1.3 for IOR C/N . These values are not significantly different from the values for the corresponding SBO and IOR, respectively, isolated from the composts listed in Table 2 (8.29 ± 0.86 for SBO C/N , and 13.9 ± 1.9 for IOR C/N).

The MW heating runs

The MW heating runs were performed with two different reactors, the CEM-Discover reactor operating with 2.45 GHz frequency and 0.3 kW applied power (runs 7-16 in Table 7), and the Sairem reactor operating with 915 MHz and 2.45 GHz frequency, and 1-2 kW applied power (runs 17-22 in Table 7). Runs 7-16 performed with CEM-Discover reactor were carried out at 114 s, upon varying l/s from 4 to 10 and T from 60 to 201°C . In these runs the following trends can be observed for the SBO yield:

- (i) no definite trend upon increasing l/s from 4 to 10 at 60°C (runs 7 through 10); the average C and N yield values over the four runs are 13.9 ± 2.3 and 16.2 ± 2.5 , respectively;
- (ii) the data at l/s 4, in the 60 - 201°C T range (Table 7, runs 7 and 11 through 13), shows that the SBO C and N yield increase upon increasing T . The linear regression of this data yields the following equation:

$$Y = a + b T \text{ (4);}$$

- (iii) the data at l/s 10 and T 60 - 169°C (Table 7, runs 10 and 14 through 16) confirms the trend of the product yield increasing with T . The linear regression of this data yields the following equation:

$$Y = a + b T \text{ (5).}$$

The constants and regression coefficient values for $Y = C$ or $N \%$ in Eq. 4 and 5 are reported in Table 6. The high correlation coefficients of Eq. 4 and 5 demonstrate that the observed yields vs. T trends are highly significant. However, based on standard error, the coefficients of the two equations do not seem significantly different, and no effect on SBO yield can be proven statistically significant at 95 % confidence level upon increasing the l/s ratio from 4 to 10.

Runs 11-17 were performed with the Sairem reactor at 60°C and variable t , l/s , MW frequency and applied power. In runs 17, 18, and 22 at l/s 4 and 60°C , no effect on SBO C and N yields is observed upon varying the contact time from 114 to 242 s. Runs 23 indicates apparently lower SBO C and $N \%$ yields at t 104 s. Runs 18 through 21 indicate a definite statistically significant trend of SBO C and $N \%$ yields to decrease upon decreasing l/s . This data fits the equation

$$Y = a + b l/s \text{ (6);}$$

the constants and regression coefficient values for $Y = C$ or $N \%$ are reported in Table 6.

The comparison of the runs performed with the CEM-Discovery reactor and with the Sairem reactor reveals that all runs performed with the Sairem reactor at 1/s 4 and 60 °C (runs 17, 18, 22 and 23) give SBO yields (18.5-24.7 C % and 23.3-30.6 N %) which are higher than those obtained in the runs (7 through 10) performed with the CEM-Discover reactor at the same pH and T conditions (10.9-13.6 C % and 13.3-18.4 N %). The different products' yields may arise from the different reactor configurations, applied power level and pulse repetition mode. However, based on the statistical data obtained for Eq 4 and 5 is doubtful that the apparent SBO yield differences between the two reactors were statistically significant. The data in Table 7 show no definite or important effect of the reaction parameters on SBO and IOR C/N. The average values of C/N, calculated over the runs 7 through 23 in Table 7, are 8.33 ± 0.47 for SBO C/N and 13.0 ± 2.0 for IOR C/N. These values are not significantly different from the average values found for the products isolated from the composts listed in Table 2, i.e. 8.29 ± 0.86 for SBO C/N and 13.9 ± 1.9 for IOR C/N. The data indicates that, under the constraints of the present work experimental conditions, no effect of t , $1/s$ and T at pH 13 is proven on the nature of the SBO product.

Comparison of microwave versus conventional heating

Comparing product types and yields for a reaction involving complex lignocellulosic materials as those listed in Table 2 is much harder than for reactions occurring for simple molecules having well defined chemical composition and structure. In this work, the C/N ratio has been used as index of the product nature. Product yields calculated on the basis of the products dry matter recovery were not used, due to the presence of the added KOH reagent. One approach was to give yields based on neat organic matter recovery. This requires measuring recovered dry matter product weight and content of volatile solids (VS). There are a few problems with using VS to assess the reaction material balance. The chemical composition of the starting materials and of the products involved in the reaction is not well known. Also, the reaction may occur with formation of products with low boiling point, which may be lost during the product drying. Thus, the reaction mass balance based on VS recovery may not account for the total VS reaction feed. A second approach was to calculate products yields based on the recovered elemental C and N. Based on Eq. 1, these elements allowed also obtain an indication of the nature of the recovered products. Under these circumstances, taking into account the high number of runs performed and the amount of analytical work required, VS were used for investigating the kinetics of the reaction performed by CON heating, whereas C and N recoveries were used for comparing CON and MW runs. The data in Table 7 shows that the SBO C and N % yield increase corresponds to the IOR C and N % decrease, and that the total C and N recoveries with the SBO and IOR products range from 71 to nearly 100 % of the C and N contained in the pristine CVD. Within the constraints of the complexity of the chemical nature of the investigated pristine material and of the hydrolysis products, these features are according to the best reasonable expectations and support the methodological approach taken in this work, as capable to give reliable process data accounting for the reaction total material balance.

Based on Table 7 C and N % recoveries, the comparison of MW and CON heating may be readily appreciated by Fig. 3. The Figure reports three groups of runs, each characterized by the same $1/s$ and T values, i.e. runs 3, 7, 17 and 18 in the first group, runs 4 and 11 in the second group, and runs 5, 6.6 and 14 in the third group. It shows no important SBO C and N % yield difference between the Sairem MW and the CON reactors, but apparently lower yields by the CEM-Discover MW reactor compared to the Sairem and CON reactors. The statistical data obtained by fitting the experimental results collected from the runs performed in the CEM-Discover (Eq. 4 and 5, and Table 6) does not allow to prove that the apparent yield difference between the two MW reactors are significant at 95 % confidence level. This situation arises from the relative high standard error

of the Equations' coefficients. The high values of the standard error in Table 6 comprise the variability contributed by a number of factors, such as the CVD material homogeneity, the products separation, isolation and analytical procedure, and the reproducibility of the MW and CON reactor systems performance. Notwithstanding these limitations, the most evident undoubted result is that similar product yield and type can be obtained by MW heating with a solid/liquid contact time about 2 orders of magnitude shorter than by CON heating. The different products' yields obtained by the two MW reactors, if real, may arise from the different power level and pulse width modulation applied by the two systems. Enhanced reaction yields upon increasing the microwave irradiation power have been reported also for other reactions and materials.²⁹

Overall, the data shows that it is possible to achieve high yields of soluble valuable products by hydrolysis of recalcitrant lignocellulosic matter, amounting to about 49 % of the starting C and/or 61 % N (Table 7, run 6.6) by CON heating at relatively low temperature ≤ 100 °C. However, Eq. 3-5 indicate a strong effect of temperature on SBO yields. Thus, the effect of temperature above 100 °C needs to be further investigated for the CVD hydrolysis carried out both in the CON reactors and in the MW reactors operating at 1-2 kW applied power. The collected data indicate that the reaction temperature in the 22-200 ° does not affect the products C/N values. The average C/N values of the SBO and IOR products obtained by CON heating runs 1 through 6.6 (8.69 ± 0.20 for SBO C/N and 14.4 ± 1.3 for IOR C/N), are not significantly different from the values for the corresponding SBO and IOR, respectively, which are calculated for the MW runs 7 through 23 (8.33 ± 0.47 SBO C/N, and 13.0 ± 2.0 IOR C/N) and for the composts' isolated SBO and IOR listed in Table 2 (8.29 ± 0.86 for SBO C/N, and 13.9 ± 1.9 for IOR C/N). Further work should be carried out to assess the optimum MW frequency and power level and pulse width modulation^{29,30} for the hydrolysis of CVD.. The effect of temperature in the 100-200 °C range needs to be investigated for both the MW and CON reactor systems. Replicate runs for each experimental condition may allow more reliable statistical analyses. This appears strictly necessary before a sound comparative evaluation was made between MW and CON heating for each specific material and reaction medium.

Potential scalability of laboratory research results to industrial level

Parallel to product yields in the higher temperature range, the potential scalability/viability of the results to industrial level is another important issue in comparing the CON and MW assisted hydrolysis of the investigated biowastes. Undoubtedly that data in Table 7 prospect that, aside from the optimum MW frequency, and power level and pulsing mode applied,^{29,30} to be assessed by further work, an MW reactor with about 2 order of magnitude smaller size may allow to achieve the same SBO production rate as a CON heated reactors. However, the size benefits of the MW reactors may be offset by their capital cost. This can be up to ten times higher than that of conventionally heated reactors. Equipment size can be reduced through development of a continuous process. This is highly feasible with the MW reactors by virtue of the reduced reagents contact time. Hereinafter, capital costs for the hydrolysis of CVD performed by CON and MW heating are compared based on the average 25 % yield of the soluble organic C recovered with the SBO product at 60 °C, respectively obtained by CON heating for 240 minutes liquid-solid contact time (Table 7 run 3) and by heating with the MW reactor operating at 915 MHz, 1 kW applied power and 242 s contact time (Table 7 run 17). An SBO production capacity equivalent to 63 kg h^{-1} of soluble organic C is assumed, corresponding to 150 kg h^{-1} of SBO dry matter containing 41 % organic C. This will require feeding approximately 5 tons h^{-1} liquid-solid slurry containing 20 % CVD dry matter with 23 % organic C content. Based on the contact time, in case of continuous operation, the required reactor volumes, filled up at 75 % total capacity, will be 27 m^3 for the CON heated reactor and 0.45 m^3 for the MW reactor. A commercial 450 L MW reactor for the hydrolysis

of the herewith investigated CVD material is available from Sairem for about 600 kEuro. The cost of a 27 m³ CON reactor is estimated about ten times lower. The data shows that equipment is available to scale the MW assisted hydrolysis to industrial level. However for the specific CVD hydrolysis the high MW reactor cost may not justify using MW instead of CON heating. Microwave reactors are more competitive in case of reactions yielding thermolabile products. In these cases the need to reduce the reaction time may be the main reason for choosing MW rather than CON reactors. This does not seem to be the case with the CVD SBO. This product is obtained from mature compost containing thermodynamically stable aromatic C moieties. Products obtained from other fermented and non fermented as collected biowastes may be less stable than CVD SBO. Therefore, further investigation on MW assisted hydrolysis should still be carried out for other biowaste materials. Results from other studies are available in literature which show that soluble bio-organic substances, having the same functional groups as the CVD SBO, although in different mole ratios, may be obtained through the hydrolysis of non fermented as collected municipal food wastes³¹ and post harvest tomato plants.³² These papers point out that the SBO chemical structure and properties depend both on the type and on the biochemical pre-treatment of the sourcing biowaste. For example the biochemical pre-treatment of the biowaste is reported to change significantly the nature of the pristine native organic matter, whereby the oxidation degree of the SBO organic matter isolated from the fermented biowaste results higher upon increasing the fermentation time of the sourcing material.³¹ This data points out that biowastes of urban and agriculture source may provide a wide range of bio-based products differing for chemical composition and solubility properties which can be further developed and tailored for specific uses in a variety of sectors of the chemical market. Undoubtedly, a process feasibility study should be carried out for each biowaste type. This would allow to compare the results, the economical benefit and feasibility of the present work dealing with fermented urban biowastes with the process dealing with different types of non fermented as collected biowaste. This approach would certainly contribute to develop new green processes and products. Also, by integrating chemical and biochemical processes, several biorefinery configuration could be developed where the as collected biowaste chemical treatment could be carried out before and/or after the biochemical treatment in order to optimize products yield and quality, and processing costs.

Conclusion

It is shown that the recalcitrant lignin fraction of the investigated five fermented urban biowastes may be converted to added value soluble lignin-like products in high yields by hydrolysis at alkaline pH. The hydrolysate products are mixture of complex polymeric molecules which maintain the memory of C type and functional groups moieties of the cellulose, hemicelluloses, lignin, proteins, and fats' proximates of the pristine fermented biowaste materials. The process feasibility study carried out for the CVD compost case study yields the following three important results: (i) hydrolysis carried out by MW and CON heating seems not to affect significantly the product yield and quality; (ii) the rate of the reaction performed by MW heating appears 1-2 orders of magnitude higher than that by CON heating; (iii) based on equipment cost, process scalability to industrial level appears more convenient using CON rather MW reactors. However, many variables connected to the reactor configuration and the type of biowaste to be processed need to be further investigated before assessing definitely which heating mode is more viable for the hydrolysis of biowastes.

Experimental

Materials

The fermented biowaste materials reported in the Introduction section were processed in a pilot production facility comprising a 500 liter capacity reactor. The solid material was treated under stirring with alkaline water at 4 ml g⁻¹ liquid/solid and 0.02 w/w KOH/solid ratios at 60 °C for 4 h. The reaction mix was allowed settling to separate the supernatant liquid containing the soluble hydrolysate (SBO) fraction from the solid IOR residue. The IOR residue was washed once with fresh water at 4 ml g⁻¹ added water/IOR ratio. The total collected liquid phase was centrifuged to separate fine solid particles, and run through a 5 kDa cut off ultrafiltration polysulphone membrane. The membrane retentate containing the SBO hydrolysate and the IOR solid product were dried in ventilated oven at 60 °C. The final dried products were analyzed according to previously reported methods⁹ and yielded the analytical values reported in Table 2-5.

Hydrolysis performed in lab equipment by conventional heating

The reaction was performed in a two necks 2 L round bottom flask equipped with a reflux condenser, magnetic stirrer and electrical heating mantle. Usually, the runs were performed using 300 g CVD samples and 1.2 L water, or 100 g CVD sample and 1.2 L water, for the reactions performed at 4 or 10 solid/liquid ratio. KOH pellets were added to the reaction mix until pH 13 was reached. The reaction was carried out for 4 h. Afterwards, the whole content of the reaction flask was centrifuged to separate the solid and the liquid fractions. The two fractions were weighed and dried. The dry matter weight was recorded. The dried samples were analyzed for the content of volatile solids (VS), C and N. In the runs dedicated to the investigation of the effect of the solid/liquid contact time, samples of 9-10 g were withdrawn from the solid-liquid mix at time intervals and centrifuged to separate the solid and the liquid fractions. The separated solid and liquid phases were worked and analyzed as above. In all cases, the analytical data and relative amounts obtained for the soluble (SBO) and insoluble (IOR) hydrolysate were used to calculate the VS, C and N % w/w yields relatively to the starting amounts charged with the pristine CVD sample.

Hydrolysis performed in MW reactors

Three different MW batch systems were used, i.e. a CEM-Discover SP at 2.45 GHz made by CEM, Matthew, NC, and a Monomode set-up at 915 MHz and a Minilabotron 2000, multimode cavity at 2.45 GHz made by Sairem, Lyon. The Discover SP is a mono mode microwave system operating with a frequency of 2.45 GHz. The microwave reaction tube capacity is 35mL, in which 2g of CVD was used. The initial microwave power of 300W was used to heat up to the target temperature 60/200°C and then during the holding period, varying amounts of microwave power were used to maintain the temperature at the target temperature for 114 seconds. The Sairem systems operated with MW generators 915 MHz and 2.45 GHz 1-2 kW, respectively. In both cases, the reactor of 2 L capacity was charged with 300 g of CVD, and operated at 60 °C. At the end of each MW run, the whole reactor content was withdrawn, centrifuged and analyzed as described for the conventional heating runs.

Analyses

Elemental analysis of C and N was performed utilizing Exeter Analytical (Warwick, UK) CE440 Elemental Analyzer (calibrated against acetanilide with s-benzylthiuronium chloride internal standard). Volatile substances (VS) were analyzed through Netzsch STA 409. The samples were heated to a target temperature of 650 °C at a heating rate of 10 °C/min, whilst applying an air purge of 100 mL min⁻¹. During the process weight (mg) and heat flow (mW) were recorded at a rate of 1

data point per 1°C rise. The resulting data between 105 to 650 °C was assumed to be the yield of volatile substances for each sample. Molecular weights were determined by size exclusion chromatography coupled with an online multiangle light scattering detector. The C types and functional group content (Table 4 and 5) was determined through a combination of analytical data obtained by ¹³C-NMR spectroscopy, potentiometric titration, and microanalysis. All analytical experimental details have been previously reported.⁹ Data fitting was performed using originpro 8 software.

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Table 1 Analytical data (% w/w) according to the methods by A.O.A.C. (2000) for SBO obtained by conventional heating.

	SBO				
	FORSUD	CV	CVD	CVDF	CVF
H ₂ O	1.00	2.34	3.03	0.53	1.00
Crude protein	44.7	18.0	30.1	28.7	30.0
Crude fat	0.24	0.07	0.04	0.08	0.10
Acid detergent fiber	16.0	52.4	53.7	59.5	54.8
Lignin	13.4	33.8	37.1	22.2	31.5
P	0.40	0.27	0.32	0.56	0.37

Table 2 VS and elemental C and N for starting digestate (FORSUD) and composts (CVDF, CV, CVD and CVF), and for SBO and IOR hydrolysates obtained by conventional heating.

Samples	VS %	C%	N%	C/N
FORSUD	65.5±1.0	29.99±0.20	3.81±0.12	7.87
FORSUD SBO	84.6±1.5	45.07±0.12	7.87±0.12	5.73
FORSUD IOR	51.0±0.6	27.68±0.08	1.80±0.05	15.38
CVDF	40.6±0.5	24.36±0.16	2.25±0.11	10.83
CVDF SBO	72.7±0.8	35.47±0.09	4.34±0.17	8.17
CVDF IOR	22.4±0.03	11.72±0.22	1.02±0.05	11.49
CVF	45.5±0.6	22.85±0.29	2.36±0.06	9.68
CVF SBO	71.8±1.1	37.35±0.38	4.80±0.07	7.78
CVF IOR	42.2±0.8	22.97±0.82	1.57±0.06	14.63
CVD	43.9±0.7	27.07±0.78	2.45±0.07	11.05
CVD SBO	71.7±0.8	37.51±0.04	4.89±0.03	7.67
CVD IOR	43.2±0.5	22.11±0.24	1.64±0.01	13.48
CV	42.9±0.6	22.43±0.42	1.91±0.03	11.74
CV SBO	72.1±1.1	38.25±0.09	4.01±0.03	9.54
CV IOR	28.7±0.4	18.44±0.67	1.15±0.09	16.03

^aConcentration values referred to dry matter: averages and standard deviation calculated over triplicates.

Table 3 Mineral elements for starting digestate (FORSUD) and composts (CVDF, CV, CVD and CVF), and for SBO and IOR hydrolysates obtained by conventional heating; Si, Fe, Al, Mg, Ca, K, Na as % w/w; Cu, Ni, Zn, Cr, Pb, Hg as ppm.^a

	Si	Fe	Al	Mg	Ca	K	Na	Cu	Ni	Zn	Cr	Pb	Hg
FORSUD	3.46± 0.05	0.77± 0.03	0.40± 0.02	0.88± 0.02	7.16± 0.08	0.53± 0.03	0.22± 0.02	73± 2	33± 0	263 ±6	20± 1	46± 1	0.40± 0.02
FORSUD SBO	0.36± 0.03	0.16± 0.00	0.78± 0.04	0.18± 0.01	1.32± 0.05	9.15± 0.06	0.39± 0.01	10± 1	27± 1	18± 4	11± 0	44± 2	0.23± 0.01
FORSUD IOR	4.73± 0.03	0.48± 0.01	0.47± 0.06	1.07± 0.02	9.54± 0.05	3.44± 0.05	0.16± 0.01	66± 4	25± 1	211 ±4	16± 1	78± 1	0.60± 0.02
CVD	10.7± 0.0	1.07± 0.02	0.71± 0.03	1.12± 0.01	4.27± 0.14	1.09± 0.03	0.08± 0.01	92± 1	71± 4	199 ±4	44± 1	54± 1	0.33± 0.01
CVD SBO	2.49± 0.04	0.88± 0.02	0.60± 0.06	0.93± 0.02	4.70± 0.08	3.76± 0.07	0.17± 0.01	24± 2	97± 2	42± 2	27± 2	99± 1	0.26± 0.01
CVD IOR	12.6± 0.1	0.95± 0.01	0.75± 0.03	1.13± 0.02	4.96± 0.05	2.13± 0.06	0.07± 0.01	73± 1	61± 2	199 ±1	44± 1	54± 1	0.22± 0.02
CVDF	6.27± 0.04	1.02± 0.01	1.06± 0.02	0.83± 0.01	3.23± 0.05	1.32± 0.03	0.07± 0.01	89± 1	53± 1	211 ±3	41± 1	6±1	0.47± 0.01
CVDF SBO	0.92± 0.03	0.53± 0.02	0.44± 0.02	0.49± 0.01	2.59± 0.03	5.49± 0.04	0.15± 0.01	21± 1	71± 0	35± 3	30± 1	75± 1	0.45± 0.02
CVDF IOR	7.68± 0.06	1.23± 0.03	1.05± 0.01	1.15± 0.02	3.20± 0.03	1.32± 0.02	0.04± 0.01	49± 2	70± 1	160 ±2	58± 1	37± 2	0.27± 0.02
CV	12.1± 0.1	1.03± 0.02	0.59± 0.01	1.67± 0.25	4.86± 0.61	1.18± 0.07	0.06± 0.01	73± 1	100 ±3	157 ±13	49± 1	43± 2	0.31± 0.01
CV SBO	2.55± 0.01	0.77± 0.04	0.49± 0.04	1.13± 0.06	6.07± 0.38	3.59± 0.21	0.16± 0.01	20± 4	92± 1	25± 1	19± 1	85± 1	0.15± 0.02
CV IOR	15.0± 0.3	1.10± 0.05	0.67± 0.01	1.45± 0.01	4.19± 0.09	1.49± 0.02	0.06± 0.01	51± 3	102 ±3	123 ±3	34± 1	39± 1	0.07± 0.01
CVF	12.5± 0.1	0.98± 0.02	0.56± 0.08	1.20± 0.02	4.26± 0.03	1.02± 0.04	0.08± 0.01	90± 1	75± 1	209 ±1	41± 2	59± 1	0.46± 0.04
CVF SBO	2.45± 0.01	0.83± 0.01	0.48± 0.03	1.00± 0.01	4.88± 0.14	3.54± 0.02	0.17± 0.01	25± 2	79± 1	45± 8	21± 1	93± 2	0.36± 0.04
CVF IOR	11.1± 0.0	0.79± 0.01	0.66± 0.08	0.98± 0.01	4.43± 0.01	2.41± 0.06	0.07± 0.00	83± 3	59± 1	193 ±6	42± 1	56± 1	0.28± 0.01

^aConcentration values referred to dry matter: averages and standard deviation calculated over triplicates.

Table 4 C types and functional groups^a concentration as mole/mole % of total organic C for starting digestate (FORSUD) and composts (CVDF, CV, CVD and CVF) and for SBO and IOR hydrolysates obtained by conventional heating.

	Cal	OMe + NR	OR	OCO	Ph	PhOY	COW	CO	X ^b
FORSUD	33.60	9.10	26.61	5.99	8.94	4.27	10.53	0.97	5.09
FORSUD SBO	43.38	9.86	14.01	3.37	9.60	3.23	15.89	0.66	3.88
FORSUD IOR	50.80	5.52	18.95	4.00	8.54	3.28	7.23	1.68	7.84
CVDF	32.86	8.33	23.85	6.34	12.30	6.73	8.21	1.37	6.04
CVDF SBO	36.90	7.24	13.22	4.18	13.39	6.84	13.53	4.69	4.81
CVDF IOR	31.70	8.43	24.58	6.14	11.49	7.23	7.74	2.68	6.18
CVF	31.13	8.15	26.93	6.20	12.03	6.13	7.77	1.66	6.28
CVF SBO	36.64	7.62	17.16	5.32	13.65	6.94	11.68	1.00	5.18
CVF IOR	26.68	8.61	31.19	8.37	13.54	6.03	4.89	0.70	7.41
CVD	37.25	9.75	28.14	4.35	8.03	5.20	6.67	0.62	6.09
CVD SBO	40.90	7.34	14.18	3.85	12.27	5.97	12.92	2.56	4.93
CVD IOR	31.73	9.39	29.32	6.39	9.78	6.21	5.87	1.31	6.55
CV	32.86	8.33	23.85	6.34	12.30	6.73	8.21	1.37	6.04
CV SBO	36.90	7.24	13.22	4.18	13.39	6.84	13.53	4.69	4.81
CV IOR	31.70	8.43	24.58	6.14	11.49	7.23	7.74	2.68	6.18

^aAliphatic (Cal), aromatic (Ph), methoxy (OMe), carboxyl (COW, W = COO⁻, O=C-OR, O=C-N), ammine (NR, R = H and/or alkyl), alkoxy (RO), phenol and/orphenoxy (PhOY, Y = H, R, Ph) and anomeric (OCO) C atoms.

^bTotal C/(OMe + NR + COX) C

Table 5 Data^a for SBO obtained by conventional heating: breakdown of OMe + NR, PHOY and COW Table 4 values, and molecular weight.

	Concentration as mole/mole % of total organic C.						M _w (kDa)	M _w /M _n
	NR	OMe	PhOH	PhOY	COOH	CON		
FORSUD SBO	7.04	2.82	2.15	1.08	6.95	8.94	164	1.93
CVDF SBO	7.24	0.00	5.13	1.71	12.18	1.35	75	1.53
CVF SBO	2.86	4.76	3.97	2.97	11.68	0.00		
CVD SBO	7.34	0.00	5.97	0.00	9.95	2.97		
CV SBO	7.24	0.00	4.89	1.95	12.49	1.04	80	3.36

^aWeight (M_w) and number (M_n) average molecular weight, and dispersivity index (M_w/M_n). Other legends as in Table 4.

Table 6 Results of the regression analysis of the data (mean ± standard error) in Fig. 1 and 2, and Table 5, according to Eq. 2-6; r = correlation coefficient.

	a	b	r
Eq. 2, c = 4.58 ± 1.40	0.0249 ± 0.0069	0.156 ± 0.020	0.8912
Eq. 3, Y = C %	13.87 ± 2.05	0.23 ± 0.03	0.98
Eq. 3, Y = N %	16.63 ± 1.86	0.30 ± 0.03	0.99
Eq. 4, Y = C %	4.34 ± 5.08	0.160 ± 0.037	0.95
Eq. 4, Y = N %	2.81 ± 7.33	0.208 ± 0.053	0.94
Eq. 5, Y = C %	3.33 ± 10.25	0.237 ± 0.081	0.90
Eq. 5, Y = N %	1.26 ± 11.0	0.283 ± 0.087	0.92
Eq. 6, Y = C %	- 2.11 ± 1.79	6.81 ± 0.65	0.99
Eq. 6, Y = N %	2.95 ± 2.31	8.72 ± 0.84	0.99

Table 7 Data for the alkaline hydrolysis of CVD yielding water soluble (SBO) and insoluble (IOR) products.

Heating mode ^a /run number	Reaction parameters				Products' yields based on C and N w/w % recoveries in the SBO and IOR dry matter relative to pristine CVD dry matter						Products quality C/N index	
					SBO C	IOR C	Total C	SBO N	IOR N	Total N		
	pH	l/s ^b	T (°C)	t ^c							SBO	IOR
CON/1	13	4	22	240 min	20.1	64.6	84.5	23.5	50.4	73.9	9.24	13.8
CON/2	13	4	40	240 min	23.1	66.4	89.6	28.4	49.7	78.1	8.84	14.5
CON/3	13	4	60	240 min	25.6	54.5	80.1	32.3	41.6	74.0	8.56	14.1
CON/4	13	4	100	240 min	38.1	39.7	77.8	47.1	24.2	71.2	8.76	17.7
CON/5	13	10	100	240 min	42.3	57.2	99.5	52.6	44.4	96.9	8.69	13.9
CON/6.1	13	10	100	5 min	17.4	41.1	58.5	22.1	36.1	58.2	8.52	12.3
CON/6.2	13	10	100	10 min	28.4	41.5	69.6	35.6	33.8	69.4	8.65	14.4
CON/6.3	13	10	100	15 min	32.6	42.8	75.4	40.9	34.3	75.2	8.61	13.5
CON/6.4	13	10	100	100 min	38.6	39.3	77.8	48.8	29.8	78.5	8.56	14.5
CON/6.5	13	10	100	240 min	40.4	35.1	75.6	45.8	24.3	70.1	8.56	15.1
CON/6.6	13	10	100	240 min	48.8	47.9	96.7	61.0	34.7	95.7	8.65	14.9
MWG/7	13	4	60	114 s	15.4	120	135	18.1	90.8	109	7.89	12.3
MWG/8	13	6	60	114 s	10.9	80.7	91.6	13.3	57.8	71.1	7.63	12.9
MWG/9	13	8	60	114 s	15.8	62.5	78.3	18.4	34.2	52.6	7.95	16.9
MWG/10	13	10	60	114 s	13.6	105	119	14.9	81.1	96.0	8.43	11.9
MWG/11	13	4	100	114 s	16.5	89.4	106	17.5	63.7	81.2	8.76	13.0
MWG/12	13	4	150	114 s	31.8	53.9	85.7	38.1	34.0	72.1	7.71	14.6
MWG/13	13	4	201	114 s	35.3	24.8	60.1	43.6	21.2	64.8	7.50	10.8
MWG/14	13	10	100	114 s	32.0	43.0	75.0	33.0	29.5	62.5	8.97	13.5
MWG/15	13	10	150	114 s	43.6	62.8	106	50.2	47.7	97.9	8.03	12.2
MWG/16	13	10	169	114 s	37.7	70.8	108	42.4	35.8	78.2	8.23	18.3
MWM1/17	13	4	60	242 s	24.7	98.1	123	30.6	87.4	118	8.71	12.1
MWM2/18	13	4	60	114 s	24.3	76.8	101	30.6	66.2	96.8	8.58	12.5
MWM2/19	13	3	60	55 s	18.8	67.2	86.0	24.5	59.6	84.0	8.31	12.3
MWM2/20	13	2	60	55 s	13.0	68.5	81.5	15.9	66.2	82.1	8.80	11.2
MWM2/21	13	1	60	55 s	3.57	72.9	76.5	4.40	69.0	73.4	8.78	11.4
MWG1/22	13	4	60	217s	22.3	51.9	74.2	27.3	41.7	69.0	8.81	13.5
MWG2/23	13	4	60	104 s	18.5	64.9	83.3	23.3	57.5	80.7	8.56	12.2

^aConventional (CON), or microwave in CEM-Discover SP 2.45 GHz (MWG) 0.3 kW, and in Sairem 915 MHz 1 kW (MWM1) and 2 kW (MWM2) and 2.45 GHz 1 kW (MWG1) and 2 kW (MWG2) systems. ^bLiquid/solid V/w ratio.

^cContact time (t) in seconds (s) and minutes (min).

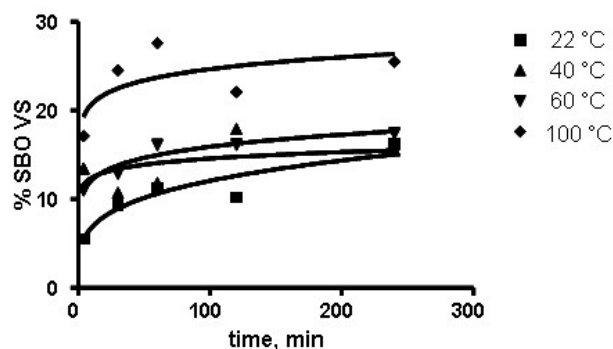


Fig.1 SBO VS w/w % yield versus at different temperature values.

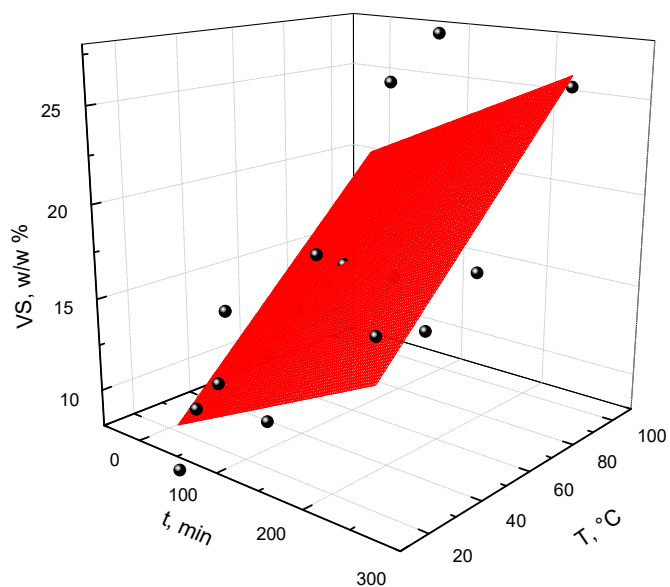


Fig. 2 Surface fitting of SBO VS w/w % yield versus t and T plot according to Eq. 2

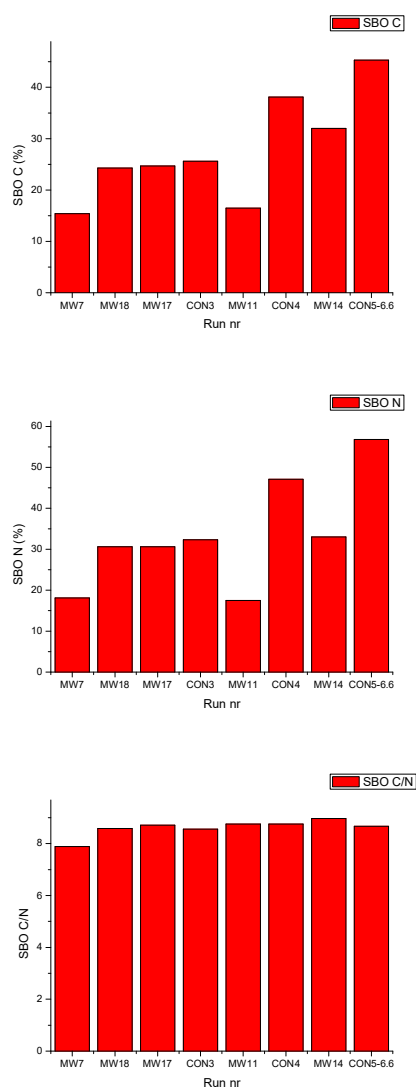


Fig. 3 Comparison of SBO C and N w/w % yields, and C/N values, obtained by MW and CON heating under the same experimental conditions: i.e. at 1/4 and 60 °C (MW7, 17, 18, and CON3), at 1/s 4 and 100 °C (MW11 and CON 4), and at 1/s 10 and 100 °C (MW14 and CON 5-6.6).

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